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KINETICS OF RAPID GAS PHASE REACTIONS
THE ADDITION OF LEWIS ACIDS TO BASES

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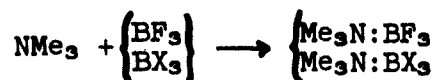
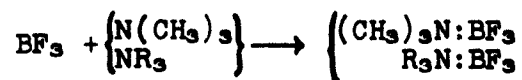
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PREFACE

Among the simplest of imaginable chemical reactions is the gas phase association of two molecular species, each of which by itself is stable under the conditions of the experiment. If this reaction is very fast, if it occurs at moderate or low temperatures (i.e., if $E_{\text{act}}/RT < 5$), and in particular, if it can be demonstrated that the rate is overall second order, but first order with respect to each species, it is presumed that the reaction proceeds via bi-molecular encounters between the reactant molecules. For such reactions, what specific chemical factors, what structural types, electron configurations, etc. determine the observed rates? How are these rates affected by substituents in parts of the molecules removed from the reactive centers? Does the ambient gas play a significant role in stabilizing the product?

The gas phase addition of Lewis acids, of which the boron trihalides are typical, to Lewis bases, of which the amines are typical, are such reactions. Since the absolute magnitudes of these rates are difficult to determine with precision over a range of pressures and temperatures, and since the primary interest lies in measurement of the effect of selected molecular parameters on the rates, this research program centered around the measurement of relative rates of addition, taking that of $[\text{BF}_3 + \text{N}(\text{CH}_3)_3 \rightarrow (\text{CH}_3)_3\text{N}:\text{BF}_3]$ as the reference value. This was done by measuring the ratios of products generated in competitive systems:



The following summary consists of three manuscripts which are reports on work done at Cornell University over a period of years. These are arranged in inverse order of performance, and are graduated with regard to stage of preparation for publication. The first paper presented (III) has been submitted and accepted for presentation at the forthcoming symposium on boron-nitrogen chemistry, U.S. Army Research Office (Durham), at Duke University, April 23-25, 1963. These papers show the development of our experimental technique and the growth of our understanding of the processes involved.

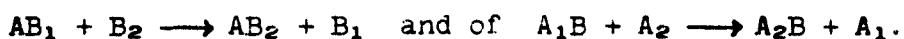
It is now evident that these reactions are far from 'simple'. Subtle and as yet incompletely investigated factors are operative during the sequence of stages through which the parent species pass on toward becoming parts of the 'adducts'. In oversimplified form these may be enumerated:

- i) Description of those encounters between A and B molecules in which their electron configurations are sufficiently perturbed so that a configuration suitable for adduct formation can result; consider dependence on relative kinetic energy, impact parameter, relative orientation, and on specific features in their intermolecular interaction potential.
- ii) For such encounters, description of the distortions which occur in their structures, particularly in the acid molecule.
- iii) Estimation of the probability for the redistribution of energy from vibrational and internal rotational modes in which large amplitudes are localized around the newly formed bond to modes in which large amplitudes appear in other parts of the molecules. Consider dependence of this stabilization on the

detailed composition and geometry of the reactants; is there a need for a third body?

iv) Estimation of the probability for the redistribution of energy from the vibrationally excited product molecule to the ambient gas, relative to the probability for the re-accumulation of energy in the newly formed bond, and consequent dissociation. Consider dependence of this de-energization on the nature and concentration of the ambient gas.

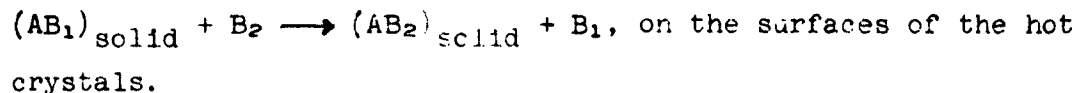
v) Estimation of the probability for the exchange reactions:



Compare these rates with that of precipitation of AB_1 and A_1B .

vi) Description of the formation of crystal embryos and nuclei, and of the rate of growth of Lewis salt crystals. Consider possible re-evaporation of reactant species from these hot crystals due to insufficiently rapid transfer of the heat of condensation to the ambient gas.

vii) Consider possible exchange reactions, such as



In the following papers attempts have been made to obtain experimental answers to some of the questions raised. We have been only partially successful, and much work remains to be done.

The last paper included in this final report summarizes computational work by Mr. Nicholas Rol. Since the association mechanism in the gas phase of aliphatic acid monomers presumably has a number of kinetic features similar to that of Lewis acid-base adduct formation, the possibility of measuring these rates

should be investigated. Mr. Rol considered the feasibility of exploiting shock tube techniques.

We here express our sincere appreciation to the Office of Naval Research for the extended support given to this project. We are particularly thankful for the personal interest shown in our research efforts.

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THE GAS-PHASE ASSOCIATION OF BORON ACIDS AND BASES. III. B₂H₆ AND BF₃ IN COMPETITION FOR N(CH₃)₃

by

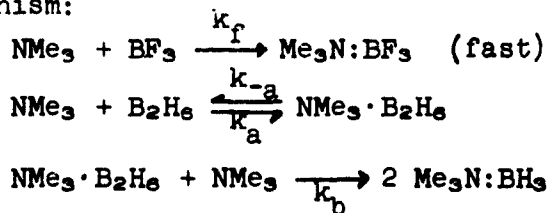
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ABSTRACT

The relative rates of addition of trimethylamine as a reference base to mixtures of boron trifluoride and diborane diluted with nitrogen have been measured at several temperatures. It was demonstrated that the pair BF₃-B₂H₆ are compatible in the sense that these gases do not react with each other to produce new substances and that the product of reaction with trimethylamine, in each case, is unaffected by the presence of the other acid. The ratio of the overall rates of addition $R_{BF_3-NMe_3}/R_{B_2H_6-NMe_3}$ increases with rising temperature, rather than decreases, as is expected were a displacement mechanism operative, such as:



Also, this ratio decreases with increasing pressure of the amine but for constant amine and acid concentrations is independent of the ambient pressure (N₂ diluent). These data can be accounted for by the mechanism:



The unstable NMe₃·B₂H₆ complex rapidly attains a steady state concentration. This leads to

$$\frac{[B_2H_6]}{[BF_3]} \frac{[Me_3N:BF_3]}{[Me_3N:BH_3]} = \frac{k_f}{2k_a} + \frac{k_f}{2K_a k_b [Me_3N]}$$

$$(k_f/k_a) = 2.2, \text{ and, } \log (k_f/K_a k_b) = -6.620 - 271.7/T$$

An analysis of these results will be presented.

INTRODUCTION

The investigation described is a continuation of our program on the determination of the relative rates of the gas phase addition of Lewis acids to bases. Our previous experiments dealt with the rates of addition of boron trifluoride, as the reference acid, to binary mixtures of ammonia, dimethylamine and trimethylamine and covered a range of temperatures, pressures and diluents. These studies indicated that such association were bimolecular and that they proceeded with practically no activation energy. The ratios of the rate constants for pressures greater than one mm are $k_{\text{NH}_3}/k_{\text{NMe}_3}$, approximately 0.1, and $k_{\text{NHMe}_2}/k_{\text{NMe}_3}$, approximately 1.1. During the past year we initiated the study of the relative rates of addition of trimethylamine, as the reference base, to binary mixtures of boron trifluoride, boron trichloride, boron trimethyl and diborane.

Correlations^{1,2} of the available kinetic data on the amine-boron trifluoride system indicate that the value for the rate constant k_f for the association reaction of an amine boron trifluoride increases as more methyl groups are substituted for the hydrogen in the amine molecule. In addition, for mono-substituted systems as the size of the alkyl group is enlarged, the rate constant appears to increase. For the pair deuterio ammonia, relative to ammonia in a reaction competing for boron trifluoride, it has been shown³ that the latter reacts approximately twice as rapidly as the former. The absolute rate constant for the addition of trimethylphosphine to boron trifluoride has also been measured⁴. In contrast to the considerable amount of

data available on the relative rates of addition of bases to boron trifluoride, there is a paucity of information on the relative rates of addition of various acids to a reference base such as trimethylamine. The kinetics of addition of diborane to phosphine and of diborane to carbon monoxide have been studied^{5,6}. As yet, the relative acidity of boron trichloride and boron trifluoride as Lewis acids has not been determined. Early data suggests that the boron trifluoride is the weaker electron acceptor^{7,8,9}. The fact that gaseous boron trichloride replaces boron trifluoride from its trimethylamine salt is the basis for Dutton's argument that the trichloride is the stronger acid.

Because of their very rapid rates, addition reactions between Lewis acids and bases are diffusion controlled. To measure the absolute rates of these reactions one must use a flame diffusion technique such as has been developed by Kistiakowsky and coworkers^{10,11,12}. However, it is possible to measure the relative rates of addition by simple competitive techniques in which it is merely important to establish that the observed ratios of products is not affected by local depletion in the reaction chamber. It is, of course, essential to establish that the products and the reactants are mutually compatible; i.e., that once a product salt is formed it does not further react with one of the competing reactants to alter its composition^{1,2}.

In this work we have shown first that the pairs $\text{BF}_3\text{-BCl}_3$, $\text{BF}_3\text{-BMe}_3$, $\text{BCl}_3\text{-B}_2\text{H}_6$ and $\text{BMe}_3\text{-B}_2\text{H}_6$ are not compatible. We have no information regarding the compatibility of $\text{BCl}_3\text{-BMe}_3$. However,

we have demonstrated that one can study, by such a comparative process the relative rates for BF_3 and B_2H_6 adding to trimethylamine. In mixtures of boron trifluoride-boron trichloride an equilibrium is rapidly established between the mixed halides¹³ so that one must deal with four reactants, rather than two, in a rather complex kinetic system. It also appears that in mixtures of diborane with boron trichloride and with boron trimethyl similar scrambling reactions occur. Where this may not be the case for mixtures of boron trifluoride and boron trimethyl, we have demonstrated that BF_3 displaces BMe_3 from the solid salt, $\text{Me}_3\text{N}:\text{BMe}_3$. However, the pair BF_3 - B_2H_6 , gave very interesting results.

EXPERIMENTAL PROCEDURE

The gaseous reagents used in this work were obtained in cylinders from commercial sources. Diborane, boron trifluoride and trimethylamine were purified in a distillation train but the nitrogen used as a carrier was taken directly from the cylinder. The specified purity of nitrogen was 99.996%.

Occasionally the purity of the three distilled gases was checked by scanning a sample of the gas with a Perkin-Elmer Model 21 Spectrophotometer. The infrared spectra thus obtained agreed in every respect with the spectra given in the literature.

From the purified reagents a mixture of diborane, boron trifluoride and nitrogen and a mixture of trimethylamine and nitrogen were prepared in two separate twelve liter bulbs. Only nitrogen was admitted to a third twelve liter reservoir bulb. For any ex-

periment the pressures of all three bulbs were made approximately equal. Mixing of the gases in the amine bulb was insured by spot heating the bulb with a small resistance heater at approximately 40 to 50°C for two hours before permitting the bulb to remain undisturbed overnight. A similar procedure was initially used for mixing in the acid bulb before determining the decomposition of diborane. Later, mixing in the diborane-containing bulb was insured by keeping it half immersed in ice water for two hours after which it was totally immersed and permitted to stand overnight.

With reference to Fig. 1, the bulbs were connected to a multi-way stopcock¹⁴ which had the feature of allowing either pure nitrogen or the acid and base mixtures to begin to flow simultaneously to the reaction vessel. The steady-state reaction pressure was set by the pressure in the bulbs and the size of the capillary orifices. A cross-section of the capillary unit is shown in Fig. 1. During the experiment the gases flowed through glass coils for temperature stabilization and through fritted glass plugs for better distribution before reaction. The reaction vessel was equipped with manometers to monitor the steady-state reaction pressure. Two traps were placed immediately after the reaction vessel to insure collection of all solid produced. One of these was a cold finger trap which was not only filled with liquid nitrogen but which was also surrounded with liquid nitrogen. The cold finger in the reaction vessel was likewise filled with the coolant.

Before experiment the system was evacuated to 10^{-5} mm overnight. During the experiment the reaction vessel was continually evacuated

to maintain a steady state pressure and prevent any building up of concentration due to unused acid. To initiate the experiment nitrogen was allowed to flow for a period sufficient to maintain a constant steady state pressure after which the acid and base reagents were introduced. This period depended upon the reaction pressure, being less for the higher pressure experiments. The introduction of the base and acid mixtures was simultaneous with the isolation of nitrogen flow, a characteristic feature of the multiway stopcock. After sufficient solid had accumulated to permit a good analysis, requiring a period anywhere from 2 to 90 minutes depending on the pressure, the flow process was reversed as the nitrogen served to purge unreacted reagents while still maintaining a constant steady state pressure. After this step, the multiway stopcock was closed, the coolant in the cold fingers allowed to escape and the residual gas evacuated until the pressure in the reaction vessel system was approximately 0.2mm. This final pressure was attained by opening the system to the high vacuum in stages while the coolant was evaporating since some excess acids had condensed in the traps. Thereafter, the entire reaction vessel system was filled to atmospheric pressure with nitrogen and allowed to reach room temperature.

As the entire reaction vessel system was constructed with a minimum of lubricated joints, the portion of the system containing all visible solid was broken from the rest of the system. The solid was extracted with analytical reagent grade chloroform. In the analysis of the resulting solution, aliquot portions were scanned with the Model 21 infrared spectrometer between the region of 9.5 to 11.5 μ in order to determine a relative measure of salts produced. The determination was obtained from a Beer's law cali-

bration plot.

The calibration was obtained by plotting the ratio of peak height absorptions vs molar weight ratio of trimethylamine borane to trimethylamine boron trifluoride. These salts were prepared employing the same procedure as described for carrying out the reaction rate study. However, only one acid was used at a time in the acid mixture, and whereas in the rate study the solid was extracted with solvent, the pure salts were recovered mechanically. The calibration solutions were then obtained by weighing the amounts of salts and subsequently adding the solvent. In effect, the molality of each component in the calibration solutions was known. The absorption peak heights were obtained from the 9.95μ band and the 10.94μ band for the borane and trifluoride, respectively. A fixed thickness cell of approximately 0.10 mm path was used in conjunction with a variable path length cell which compensated for the solvent.

In extracting the solid produced in the reaction rate experiments carried out at room temperature and above, it was observed that not all the solid dissolved in the chloroform; no residue was found for runs made at the lower temperatures. The quantity of the insoluble material increased as the temperature of the experiment was increased, and limited the upper temperature for this experiment to 60°C . Attempts to identify the insoluble material were unsuccessful. The side product, which was found to be soluble in water and in acetone, formed principally on the cold finger.

In one particular experiment performed at 80°C , pure trimethyl-

amine borane was prepared from the reagent gases and the major portion of the substance was recovered mechanically. (see footnote 1.). The amount of insoluble material was determined to be no more than 5% of the total amount of solid produced.

EXPERIMENTAL RESULTS

Investigations were carried out at -80° , -35° , 25° and over the region 50° - 90°C . The conditions for the experiments and results are summarized in Tables Ia through Id. The final relative rate constants are summarized in Fig. 2.

Inspection of the processed data shows a linear dependence between the ratio j/s and the reciprocal of the average steady state trimethylamine concentration. This linear dependence is shown in Fig. 2. The lines as drawn were obtained using the method of least squares. The parameters for the four linear relations are summarized in Table II. We should emphasize that j/s did not correlate with the total steady state pressure, nor with its inverse, nor with the ratio of the total pressure to that of the amine.

A plot of the log of β vs the reciprocal of the absolute temperature is shown in Fig. 3a. The method of least square gives the following relationship:

$$\log \beta = -6.620 - 271.7/T ; \quad \beta \text{ in (moles/cc)}$$

(1)

$$\langle \alpha \rangle = 2.2$$

DISCUSSION OF RESULTS

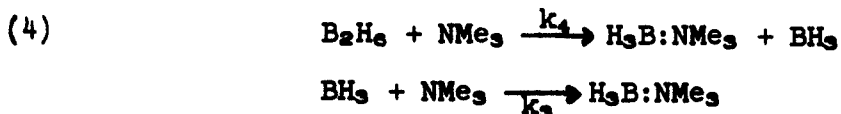
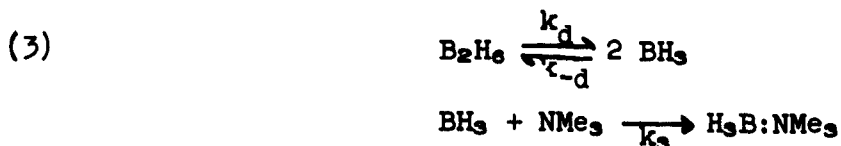
8.

Interpretation of the data for $\text{BF}_3 + \text{NR}_3$: The addition of trialkylamine to boron trifluoride, according to an inverse Lindemann-Hinshelwood mechanism¹², where the carrier gas serves as a third body for the stabilization of a product molecule, will serve as a first approximation. The production of the fluoride salt is given by

$$(2) \quad d[\text{Me}_3\text{N}:\text{BF}_3]/dt = k_f[\text{BF}_3] [\text{Me}_3\text{N}],$$

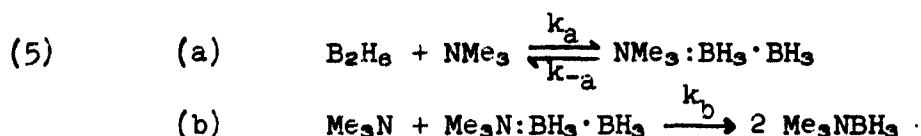
for which the high pressure limiting rate constant, k_f , has been measured¹² to be $2.8 \times 10^{12} \text{ cc mole}^{-1} \text{ sec}^{-1}$.

The reaction between trimethylamine and diborane may follow one of several mechanisms. However, it is immediately evident that the following ones are incompatible with the data:



Since the reaction between boron trifluoride and trimethylamine occurs with practically no activation energy, while in mechanism (3) the dissociation of B_2H_6 requires an increase in energy of about 28 kcal (see Footnote 2.) and in mechanism (4) we anticipate that the displacement reaction will require somewhere between 3 and 6 kcal, (see Footnote 3.) it is clear that the amount of borane salt relative to BF_3 salt should decrease as the temperature of the reaction in which the competitive process occurs is decreased. However, the inverse

9.
has been observed as shown by the slopes in Fig. 2. One must therefore find a mechanism which favors the formation of the borane salt. at the lower temperatures. We therefore propose that the reaction between the diborane and the trimethylamine occurs as follows:



Under the steady-state condition, steps (a) and (b) yield

$$(6) \quad \frac{d[Me_3N:BH_3]}{dt} = \frac{2k_a k_b [B_2H_6] [NMe_3]^2}{k_{-a} + k_b [NMe_3]}$$

With relation (2) as a reference, expression (6) leads to

$$(7) \quad \frac{[B_2H_6]}{[BF_3]} \frac{d[Me_3N:BF_3]}{d[Me_3N:BH_3]} = \frac{k_f}{2k_a} + \frac{k_f}{2K_a k_b [NMe_3]}$$

where K_a is the equilibrium constant for reaction (5a) in (mole/cc)⁻¹. (See footnote 4).

Expression (7) is of the proper functional form not only with respect to the effect of temperature but also with respect to the trimethylamine pressure dependence. The integrated form of equation (7) may be obtained under assumption that the amount of salts produced are small enough that the amount of acid used in their production remain essentially unchanged (steady-state concentration due to gas inflow). Application of the differential form interprets the real case more closely than does imposing the necessary restrictions to obtain the integrated form. Even so, in applying the differential form, an average value for the concentration of trimethylamine must be used.

Hence,

$$(8) \quad \frac{[\text{B}_2\text{H}_6][\text{Me}_3\text{N}:\text{BF}_3]}{[\text{BF}_3][\text{Me}_3\text{N}:\text{BH}_3]} = \frac{k_f}{2k_a} + \frac{k_f}{2K_a k_b [\text{NMe}_3]}$$

On comparing equation (8) with the empirical formulation of the data, $j/s = \alpha + \beta q$, one may identify α with $k_f/2k_a$ and β with $k_f/2K_a k_b$. Within the precision of the experiments α has no temperature dependence; an average value $\langle \alpha \rangle = 2.2$ is proposed. Using the above quoted magnitude for k_f one finds,

$$k_a = 6.4 \times 10^{11} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

This is the limiting rate for very high amine pressures for the formation of the 1:1 complex. At 293°K, the smoothed experimental value for $\beta = 2.94 \times 10^{-8} \text{ mole cc}^{-1}$, so that $K_a k_b = 4.8 \times 10^{19} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ at that temperature.

The temperature dependence of β is due to the non-vanishing of the sum of the enthalpy increment in (5a) and the activation energy for (5b). One may plot $\log \frac{[K_a k_b]}{T}$ vs $1/T$ as in Fig. 3b. The slope gives

$$\Delta H_a^\circ + E_b = -1.65 \text{ kcal/mole}$$

Thus, the net process in going from the reactants in (5a) to the transition state of (5b) is slightly exothermic.

The assumption of the 1 to 1 complex between trimethylamine and diborane may appear strange at first. However, some indication of the existence of the triethylamine-borane complex at -64° has been given by Brown and coworkers¹⁶ and a similar 1 to 1 complex has been

proposed by Parry and Shore¹⁷. Our kinetic data require merely that this complex be present in very small amounts during the course of this reaction.

OBSERVATIONS ON THE BCl_3 - B_2H_6 SYSTEM

We attempted to obtain an estimate of relative reaction rates of BCl_3 and of diborane with trimethylamine. When competitive kinetics experiments were run even at temperatures as low as -80°C , absorption bands appeared in the infrared spectrum of the products which were not present in the solutions of the pure salts. These peaks interfered with the analysis for the relative amounts of $\text{Me}_3\text{N}:\text{BCl}_3$ and $\text{Me}_3\text{N}:\text{BH}_3$. The spectra of the separate salts in chloroform solution were previously run and calibration curves for the mixtures were obtained. In preparing these calibration curves we demonstrated that in chloroform solution these two salts are mutually compatible. This led us to question whether any reaction took place between gaseous mixtures of BCl_3 and B_2H_6 . Two earlier works^{15,18} have shown that no reaction occurs between these acids under conditions similar to those used in this work. However, we found that a reaction did occur as evidenced by the appearance of new bands in the infrared spectrum of the mixture. The rate of appearance of the new bands were followed and the rate was determined to depend on the ratio of the diborane to boron trichloride pressures. Fig. 4 shows this conversion rate for three such ratios.

It is clear that, if one could work over a period of less than half an hour, this scrambling reaction would introduce a minimum amount of difficulty. It is therefore evident that

some displacement reaction occurs during the initial stages of the formation of the salts. Hence, the mechanism for this system is more complicated than what we have postulated and found satisfactory for the $\text{BF}_3\text{-B}_2\text{H}_6$ system. Further work on this mixture is required before conclusions regarding the relative rate constants can be obtained from our data. Compatibilities (or lack of them) for several acid systems are summarized in Table III.

ACKNOWLEDGEMENTS

The authors express their appreciation to Dr. Assa Lifshitz for partaking in discussions of this work. Also, they acknowledge with thanks the support of the Office of Naval Research.

FOOTNOTES

1. This material could be separated into a crystalline portion which deposited around the cold finger, and an 'amorphous' portion which adhered to the walls of the reaction vessel below the cold finger, down towards the reaction zone. The spectra of both these samples were identical with that of trimethylamine borane. Extractions were made of the solid remaining in the vessel, using chloroform and acetonitrile. After extraction, the residual material was recovered mechanically and incorporated in a KBr pellet. Its IR spectrum was not of $H_3B:NMe_3$, and could not be identified.

2. The imposition of a steady state condition on mechanism (3) leads to:

$$\frac{d[Me_3N:BH_3]}{dt} = \frac{k_s}{2} [Me_3N] \left\{ \left(8K_d[B_2H_6] + \frac{k_s}{k_{-d}} [Me_3N]^2 \right)^{1/2} - \frac{k_s}{k_{-d}} [Me_3N] \right\}$$

The magnitude of K_d has been given²²; on re-estimating the entropy for BH_3 , we recommend

$$\log_{10} K_d(\text{atm}) = 7.775 - 6205/T$$

The value for k_s should be temperature independent, and possibly a bit larger than k_f . For k_{-d} a value in the neighborhood of 10^{13} to 10^{14} cc mole⁻¹ sec⁻¹ is reasonable. [See, S. H. Bauer,²⁰ J. Amer. Chem. Soc., 78, 5775 (1956)]. One may therefore introduce several approximations in the above expression, to reduce the ratio of salts produced to:

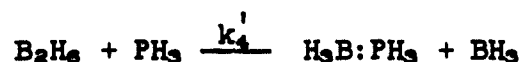
$$\frac{[B_2H_6]}{[BF_3]} \frac{d[Me_3N:BF_3]}{d[Me_3N:BH_3]} = \frac{k_f}{2k_d} [Me_3N]$$

3. The imposition of a steady state condition on mechanism (4) leads to:

$$\frac{d[\text{Me}_3\text{N}:\text{BH}_3]}{dt} = 2k_4 [\text{Me}_3\text{N}] [\text{B}_2\text{H}_6]$$

$$\frac{[\text{B}_2\text{H}_6]}{[\text{BF}_3]} \frac{d[\text{Me}_3\text{N}:\text{BF}_3]}{d[\text{Me}_3\text{N}:\text{BH}_3]} = \frac{k_f}{2k_4}$$

Now, for the reaction,



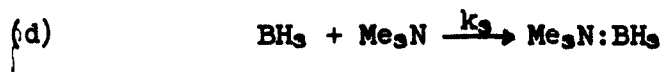
Brumberger and Marcus⁵ found $k_4' = 2.3 \text{ cc mole}^{-1} \text{ sec}^{-1}$ at 0°C .

Also, they found that the activation energy was 11.4 kcal/mole, and the steric factor was 3×10^{-5} , of the same order of magnitude as generally observed in hydrocarbon abstraction reactions. Even if one allows a factor of 10^8 for the ratio k_4/k_4' , because of the greater base strength of NMe_3 compared with PH_3 , our data are not consistent with what one would expect for such a mechanism.

4. Parallel to (5b) an additional reaction may occur



where X is any molecular species other than NMe_3



One must now introduce a steady state condition on (BH_3) . It then follows that an expression corresponding to (7) takes the form

$$(7) \quad \frac{[\text{B}_2\text{H}_6]}{[\text{BF}_3]} \frac{d[\text{Me}_3\text{N}:\text{BF}_3]}{d[\text{Me}_3\text{N}:\text{BH}_3]} = \frac{k_f}{2k_a} + \frac{k_f}{2K_a(k_b[\text{NMe}_3] + k_5[\text{X}])}$$

Under the conditions of our experiment we have demonstrated that $k_5[\text{X}]$ is not much larger than $k_b[\text{NMe}_3]$; otherwise j/s would correlate

with the inverse of the total pressure. However, it is possible that $k_s[X] \approx k_s[NMe_3]$. We could not vary the ratio of amine concentration to total pressure over a sufficient range to check this possibility. Hence, it may be that $K_a k_b \approx 2.5 \times 10^{19} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ rather than the larger value given in the text.

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TABLE Ia. TYPICAL DATA FOR KINETICS EXPERIMENTS AT(50-90°C)

	a	b	c	d	f	g	h	j	m	r	s	qx10 ⁻⁷	t°C
1.	98.4	6.3	293.5	1.7	10.2	8.5	0.113	15.62	0.029	34.48	0.55		79.8
2.	239.5	13.5	301.5	3.3	9.4	7.0	0.215	17.74	0.051	19.61	0.65		87.6
3.	178.4	10.1	301.5	2.5	8.8	8.0	0.150	17.66	0.036	27.78	0.72		91.6
4.	70.0	4.7	201.0	2.0	79.4	9.0	0.914	14.89	0.400	2.50	1.28		86.4
5.	268.5	18.7	481.5	6.8	42.5	4.0	0.900	14.36	0.266	3.76	1.25		68.3
6.	179.9	12.4	345.3	4.8	27.7	3.0	0.530	14.51	0.178	5.62	1.51	11.32	51.6
7.	126.7	8.7	262.0	3.6	13.0	8.5	0.214	14.56	0.090	11.11	1.77	22.38	50.3
8.	72.1	4.9	147.8	2.0	6.2	10.0	0.102	14.11	0.043	23.26	0.85	46.85	50.3
9.	133.0	8.6	214.1	2.8	9.2	6.5	0.184	15.46	0.061	16.39	0.80	33.01	50.0
10.	91.8	5.9	140.3	2.2	6.6	6.0	0.135	15.56	0.051	19.61	1.01	39.50	49.9
11.	63.7	4.1	97.0	1.4	0.3	61.0	0.005	15.54	0.002	500.	---		48.2
12.	59.3	3.8	89.8	1.3	0.8	17.5	0.030	15.60	0.001	1000.	---		50.0

TABLE Ib. TYPICAL DATA FOR KINETICS EXPERIMENTS (ROOM TEMPERATURE)

	a	b	c	d	f	g	h	j	m	r	s	$qx10^{-7}$
1.	168.9	29.3	321.7	15.2	11.2	5.5	0.471	5.80	0.284	3.52	1.87	6.54
2.	107.3	18.5	309.3	11.9	9.0	6.5	0.365	5.80	0.114	8.77	1.86	16.30
3.	170.5	33.3	309.0	17.6	5.6	6.5	0.400	5.12	0.200	5.00	1.40	9.29
4.	78.9	14.5	165.4	12.3	1.4	11.5	0.062	5.44	0.052	19.23	0.32	35.73
5.	70.6	13.0	148.0	11.3	1.3	11.5	0.052	5.43	0.052	19.23	0.40	35.73
6.	65.3	12.0	136.9	10.4	1.2	12.5	0.545	5.44	0.043	23.26	0.33	43.22
7.	75.6	12.8	331.0	8.6	57.0	2.5	0.439	5.91	1.228	0.81	2.45	1.50
8.	64.9	10.9	287.0	3.5	10.9	7.0	0.255	5.95	0.055	18.18	0.45	33.78
9.	156.3	14.4	318.7	4.9	9.4	7.0	0.201	10.85	0.081	12.34	0.86	22.93
10.	126.8	11.6	322.7	3.8	10.6	7.0	0.201	10.93	0.062	16.13	1.17	29.97
11.	93.5	8.5	322.5	2.9	11.8	7.0	0.166	11.00	0.051	19.61	1.00	36.44
12.	139.5	8.9	348.7	2.3	11.7	9.0	0.152	15.67	0.038	26.32	1.08	48.90
13.	129.9	7.3	320.8	1.8	11.1	7.0	0.124	17.79	0.030	33.30	0.80	61.87
14.	381.5	24.2	629.0	6.1	22.3	6.0	0.420	15.76	0.115	8.70	1.95	16.16
15.	412.7	27.2	607.8	7.4	59.2	5.0	1.128	15.17	0.416	42.40	2.40	4.46
16.	238.0	15.7	598.0	3.2	56.6	5.0	0.571	15.16	0.186	5.38	2.65	10.00
17.	152.8	20.7	326.4	0.9	7.6	8.0	0.069	7.38	0.180	5.56	—	10.33
18.	210.9	19.7	374.3	0.7	8.9	7.5	0.137	10.70	0.012	83.33	—	154.83
19.	190.3	17.5	336.0	0.5	8.7	8.0	0.200	10.87	0.008	125.0	—	232.2
20.	104.0	6.9	262.8	1.4	2.3	20.0	0.033	15.07	0.006	167.0	—	310.3
21.	85.0	5.6	214.0	1.2	1.6	71.0	0.022	15.18	0.004	250.0	—	464.5

TABLE Ic. TYPICAL DATA FOR KINETICS EXPERIMENTS AT (-35°C)

	a	b	c	d	f	g	h	j	m	r	s	qx10 ⁻⁷
1.	109.1	6.8	214.1	2.3	2.8	12.5	0.036	16.04	0.018	55.56	—	82.45
2.	96.6	5.9	210.1	1.9	10.7	6.0	0.149	16.37	0.048	20.83	4.13	30.91
3.	151.3	10.2	237.0	3.3	10.8	6.0	0.234	14.83	0.075	13.33	3.54	19.78
4.	99.2	6.4	155.4	2.2	7.0	6.0	0.144	15.50	0.050	20.00	1.74	29.68
5.	67.8	4.3	106.6	1.5	5.0	10.0	0.119	15.77	0.030	33.33	1.88	49.47
6.	251.2	18.1	486.8	7.7	35.2	4.0	0.738	13.88	0.246	4.06	4.64	6.02
7.	141.4	10.2	283.0	4.3	18.0	7.0	0.355	13.86	0.125	8.00	4.40	11.87
8.	60.7	4.4	135.0	2.2	1.6	34.0	0.024	13.80	0.013	76.92	0.85	114.15
9.	236.8	15.8	304.8	5.4	3.6	11.0	0.089	14.99	0.034	29.41	1.25	43.64
10.	197.2	13.2	258.5	4.4	2.8	14.0	0.069	14.94	0.025	40.00	1.87	59.36
11.	158.8	10.7	206.3	3.5	2.2	16.0	0.057	14.84	0.020	50.00	1.07	74.20
12.	124.2	8.4	157.8	2.7	1.6	24.0	0.044	14.78	0.014	71.43	0.83	106.00

TABLE Id. TYPICAL DATA FOR KINETICS EXPERIMENTS AT -85°C.

	a	b	c	d	f	g	h	j	m	r	s	$qx10^{-7}$
1.	51.7	4.7	252.8	1.7	8.8	7.0	0.086	11.00	0.029	34.48	2.57	40.41
2.	317.5	20.5	338.0	5.0	8.1	7.0	0.250	15.49	0.059	16.95	2.85	19.86
3.	244.6	15.8	332.6	3.9	9.1	7.0	0.218	15.48	0.052	19.23	4.20	22.54
4.	186.0	12.0	324.5	3.0	9.9	7.0	0.186	15.52	0.045	22.22	4.50	26.04
5.	283.5	19.0	498.0	6.6	34.2	5.5	0.735	14.92	0.198	5.05	4.94	5.92
6.	126.3	8.4	263.2	3.7	12.7	9.0	0.192	15.04	0.088	11.36	4.78	13.31
7.	239.0	15.0	307.5	5.2	3.6	9.0	0.086	15.93	0.032	31.25	2.53	36.62
8.	206.5	13.0	267.3	4.4	4.1	14.0	0.078	15.88	0.043	23.26	4.86	27.26
9.	164.3	10.3	212.0	3.0	3.0	12.0	0.074	15.95	0.026	38.46	2.82	45.08
10.	127.1	8.0	164.3	2.2	2.1	17.0	0.056	15.89	0.017	58.82	1.33	68.94
11.	243.9	17.1	486.0	6.3	46.0	3.0	0.841	14.26	0.285	3.51	4.06	4.11
12.	161.0	11.3	324.0	4.3	31.7	3.0	0.572	14.25	0.198	5.05	5.93	5.92
13.	107.3	7.5	198.6	3.0	4.6	12.0	0.076	14.31	0.034	29.41	3.62	34.47
14.	83.1	5.8	167.7	2.2	3.2	15.0	0.051	14.33	0.023	43.48	1.35	50.96
15.	60.6	4.2	121.1	1.4	2.1	22.0	0.036	14.43	0.013	76.92	1.42	90.15

a) pressure of diborane in the acid mixture at room temperature (mm)

b) ditto for boron trifluoride

c) total pressure in acid bulb at room temperature (mm)

d) pressure of trimethylamine in base mixture at room temperature (mm)

f) average steady-state reaction pressure during flow of Lewis reagents (mm)

g) period of Lewis reagents flow (min)

h) average partial steady-state reaction pressure (mm) of boron trifluoride

j) ratio of diborane to boron trifluoride in acid mixture

m) ditto (h) for trimethylamine

r) reciprocal of average steady-state trimethylamine pressure (mm^{-1})s) measured molar ratio of borane salt to fluoride salt, $[\text{Me}_3\text{N:BF}_3]/[\text{Me}_3\text{N:BF}_3]$ q) reciprocal of average steady-state trimethylamine concentration ($[\text{moles/cc}]^{-1}$)

TABLE II. LINEAR DEPENDENCE OF j/s ON q ($j/s = \alpha + \beta q$)
AS A FUNCTION OF TEMPERATURE

$T(^{\circ}\text{K})$	α	$\beta(\text{moles/cc})$
323	2.42	3.68×10^{-8}
298	2.17	3.11×10^{-8}
238	2.30	1.36×10^{-8}
188	1.83	1.08×10^{-8}

TABLE III
THE AVAILABLE DATA ON COMPATIBILITY OF ACID PAIRS

BF ₃	Rapid scrambling of the gas phase. (Higgins, et al 18)	BF ₃ displaces BMe ₃ from its solid salts with t _{1/2} ~ several minutes. (Price and Bauer)	Compatible (Martinez and Bauer)
BCl ₃	—	?	Gases react slowly. Chloroform solutions of pure salts are compatible. Acids attack freshly generated salts. (Martinez and Bauer)
BMe ₃	—	—	Gases react but rates may be slow enough for competitive study. (Schlesinger and Walker, 21)
BBr ₃	Scrambling of the gas phase. Equilibrium established in a few hours. (Long and Dollimore, 19)	?	Gases react slowly similar to BCl ₃ . (Schlesinger and Burg, 18)

LEGENDS FOR FIGURES

Fig. 1. Diagram of apparatus and cross-section of capillary unit.

Fig. 2. Plot of overall reaction rate vs reciprocal of trimethylamine steady state concentration for different temperatures.

$$j/s = \frac{(P_{B_2H_6})}{(P_{BF_3})} \frac{[Me_3N:BF_3]}{[Me_3N:BH_3]}$$

$$q = [Me_3N]^{-1} \text{ in (cc/mole)}$$

Fig. 3a. Plot of $\log \beta$ vs the reciprocal of the absolute temperature.

Fig. 3b. Plot of $\log [K_a k_p/T]$ vs the reciprocal of the absolute temperature.

Fig. 4. Plot of absorbance vs time for 9.12 μ band from B_2H_6 - BCl_3 reaction at room temperature for different initial pressure ratios.

$$P_{B_2H_6}/P_{BCl_3} = 26.5 \text{ for a; } 12.8 \text{ for b; } 6.6 \text{ for c.}$$

$$P_{B_2H_6} + P_{BCl_3} = 55.0 \text{ mm for a; } 44.0 \text{ mm for b; } 30.5 \text{ mm for c.}$$

